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# DETERMINATION OF Ca AND Mg BY FLOW INJECTION ANALYSIS AND ATOMIC ABSORPTION SPECTROSCOPY

by

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**ABSTRACT**

Flow Injection Technology is applied to Atomic Absorption Spectroscopy for automated Ca and Mg analysis. A rate of 120-140 samples per hour was found to be optimal. Sample volume requirements are less than 500 ul per analysis. Analysis precision is less than 2% RSD. Detection limts are well within acceptable values for Ca and Mg by AA spectroscopy. The described method of FIA controlled AA operation was found to be superior to currently used WQNL AA procedures for the given parameters.

RESUME

On a appliqué la technologie de l'analyse en flux continu à la spectrométrie d'absorption atomique pour l'analyse automatisée du calcium et du magnésium. Le taux optimal semble être de 120 à 140 échantillons par heure. On peut effectuer l'analyse d'échantillons dont le volume est inférieur à 500 ul avec une erreur relative de moins de 2 p. 100 de l'écart-type. Les seuils de détection dépassent nettement les valeurs acceptables pour la spectrométrie d'absorption atomique du Ca et du Mg. Cette méthode basée sur l'injection en flux continu permet d'obtenir en spectrométrie d'absorption atomique des résultats supérieurs à ceux que peut espérer le LNQE en utilisant des méthodes conventionnelles pour l'analyse des paramètres visés.

## INTRODUCTION

Flow Injection Analysis (FIA) has been adapted for automated sample delivery in Atomic Absorption Spectroscopy (AA). It entails automated insertions of discrete but small (200 ul) volumes of the sample into a constantly flowing lanthanum reagent stream, which is pumped directly into the nebulizer. This allows Ca and Mg analysis with high precision (less than 2% RSD), low detection limits (2 and 1 ppb respectively) at speeds of 120 to 140 samples per hour. The interpretation of the results is presently limited to reading and comparing of relative peak heights from recorder charts. The introduction of a microprocessor or computer control will further enhance the advantages of this FIA controlled AA operation.

## EXPERIMENTAL SECTION

### Apparatus

A block diagram of the system is shown in Figure 1. The equipment used consisted of a Perkin Elmer Model 403 AA Spectrophotometer interfaced to a Lachat Quik Chem FIA System consisting of Model No. 1000-600 Dual Valve Injection Module, Model No. 1000-200 Peristaltic Proportioning Pump, Model 1000-100 Automatic Sampler and a Model 1000-150 Sampler/Valve Controller.

**Reagents**

1. Lanthanum chloride stock solution. Weigh out 58.6 g lanthanum oxide ($La_2O_3$) and transfer to a 1000 ml beacker. Add about 500 ml deionized water, followed by 100 ml concentrated HCL. Heat and stir the mixture until the salt dissolves. Cool, filter into a 1000 ml flask and make up to mark with deionized water.
2. Lanthanum chloride working solution. Prepare by diluting the lanthanum chloride stock solution by a factor of 1:20 with deionized water.
3. Stock calcium and magnesium solutions. See Water Quality Methods Manual for instructions on preparation of the solutions.
4. Deionized water (wash).

**SYSTEM ASSEMBLY**

The FIA manifold is assembled according to Figures 1 and 2. Connections to the valve are made via the "screw-in tubing connectors". All tubing connections between the pump, the sampler, the valve unit and the nebulizer must be kept to a minimum, to prevent zone spreading. Also carefully read all Lachat Operating Manuals and Appendix I of this Manual.

**OPTIMIZATION OF THE METHOD**

For successful operation of FIA controlled AA spectroscopy, the AA operation must be optimized, as described in the Perkin Elmer Manual. See also Appendix I - "Flow Injection System", sections 1, 2, 3, 4 and 5 and "Changes in AA operation due to FIA interface".

In essence, what needs to be controlled is the time the sample "plug" requires to fill the sample loop in the "Loading Cycle". It is the time it takes for the full content of the sample loop to be injected into the reagent stream in the "Injecting Cycle". Furthermore, consideration must be given to the "Wash Cycle" which introduces a "wash plug", bracketed by two "air plugs" and which are also in the path between sample tray and the sample loop, effectively separating the individual "sample plugs". The timing has to be such that neither the air nor the wash are in the sample loop during the "Injecting Cycle". This is easily tested by observing the lead bubbles as the sampler begins the wash cycle. The wash cycle coincides with the "Inject Cycle". As the sample loop injects its content into the reagent stream, the first "air" plug travels towards it, followed by the "wash" and the second "air" plug. But before the three "plugs" get to the loop, the valve must switch back to "Load". The three "plugs" must be allowed to pass through the loop and out into waste before the next "Inject" can be activated. The sample, once it is injected into the reagent stream, continues towards the

nebulizer. The precise timing of the "Load" and "Inject/Wash" cycles is extremely important for optimum performance.

An "example" timer setting is 22 seconds for the Load position and 8 seconds for the Inject/Wash position. This coincides with a pump setting of 80. This is also a setting, where more than one sample is in the system at one time.

**OPERATION**

1. Assemble the FIA part of the system according to instructions given in Appendix I.
2. Set up and time the AA spectrophotometer to the parameter at hand according to the Perkin-Elmer Manual.
3. Connect the nebulizer to the FIA unit via the aspirator tubing and run a test solution (standard) through the system to optimize the nebulizer, flame and burner settings for the concentrations that are expected, including the recorder range.
4. Fill the sampler tray. The first three cups should be blanks, followed by standards and samples.
5. Begin analysis.

At the end of the run, the system must be flushed out by running distilled water through all tubings to remove lanthanum. The nebulizer must be disassembled and rinsed to prevent acid corrosion.

**ANALYSIS OF SAMPLES**

A total of 600 "high" and "low" level Calcium and Magnesium samples were analyzed by WQNL, using automated AA sample aspiration from a sample tray, but manual sample preparation. The same samples were analyzed by FIA - AA spectroscopy. The original tabulation of the results is given in Appendix II.

**COMPARATIVE RESULTS**

The two methods were compared by the following statistical means: control runs of samples, recovery tests (spiking), duplication within and between SD pairs and by SD and RSD % from replicates from "high" and "low" levels of calcium and magnesium. Summaries of the results are given in Tables 1 and 2.

**TABLE 1. COMPARATIVE TABLE FOR MAGNESIUM**

A statistical evaluation of Mg results obtained by both the FIA controlled AA operation and WQNL AA procedure.

| | < 20 ppm | | < 2 ppm | |
|---|---|---|---|---|
| | FIA | WQ | FIA | WQ |
| Control Run | 6.1 | 6.2 | 0.1<br>0.83<br>1.36 | 0.09<br>0.79<br>1.29 |
| Recovery % | 102 | 98 | 106 | 97 |
| Duplicates within (SD) 10x | 0.07 | 0.21 | 0.004 | 0.018 |
| Duplicates between (SD) 10 x | 0.09 | 0.4 | 0.003 | 0.003 |
| Replicate levels | 8.2<br>(31x) | 8.1<br>(31x) | 0.249<br>(27x) | 0.519<br>(27x) |
| Replicates RSD % | 1.0 | 1.4 | 0.8 | 1.2 |

A total of 300 Mg samples were analyzed.
FIA sampling rate: 120 - 140 s/h.
WQL sampling rate: A semi-automated "manual" procedure - the rate is variable and difficult to estimate.

**TABLE 2. COMPARATIVE TABLE FOR CALCIUM**

A statistical evaluation of Ca results obtained by both the FIA controlled AA operation and WQNL AA procedure.

| | < 100 ppm | | < 10 ppm | |
|---|---|---|---|---|
| | FIA | WQ | FIA | WQ |
| Control Run | 28.5 | 28.2 | 0.44<br>3.71<br>7.34 | 0.46<br>3.73<br>7.29 |
| Recovery % | 100 | 101 | 100 | 99 |
| Duplicates within (SD) | 0.43 | 0.28 | 0.018 | .03 |
| Duplicates between (SD) | 0.52 | 0.68 | 0.024 | .02 |
| Replicate levels | 38.5<br>(31x) | 38.8<br>(31x) | 0.59<br>(27x) | 0.45<br>(27x) |
| Replicates RSD % | 0.3 | 0.9 | 2.4 | 1.7 |

A total of 300 Ca samples were analyzed.
FIA sampling rate: 120 - 140 s/h.
WQL sampling rate: A semi-automated "manual" procedure - the rate is variable and difficult to estimate.

## APPENDIX I

This manual is intended to assist the operator in understanding the Lachat FIA unit as it applies to AA operations. However, a more detailed explanation of FIA principles itself, may be obtained from the literature. Carefully read all Lachat manuals, especially the Operating Instructions "Injection Module - Dual Valve, Module No. 1000-600".

It is important to realize that the sample in this sysem is aspirated through the valve into the sample loop, involving ports 6, 1, 4 and 5 in the Load position ("OFF" on the timer, green LED on the valve unit) and swept out into the reagent stream by the carrier during the INJECT position (red LEDs on timer and valve units), involving ports 2, 1, 4 and 3. The sample loop is connected to ports 1 and 4.

The schematic in Figure 1 represents a block diagram of the system.

### REAGENTS

1. Stock Ca and Mg solutions.
2. 0.25% lanthanum solution
3. Distilled water (wash and carrier).

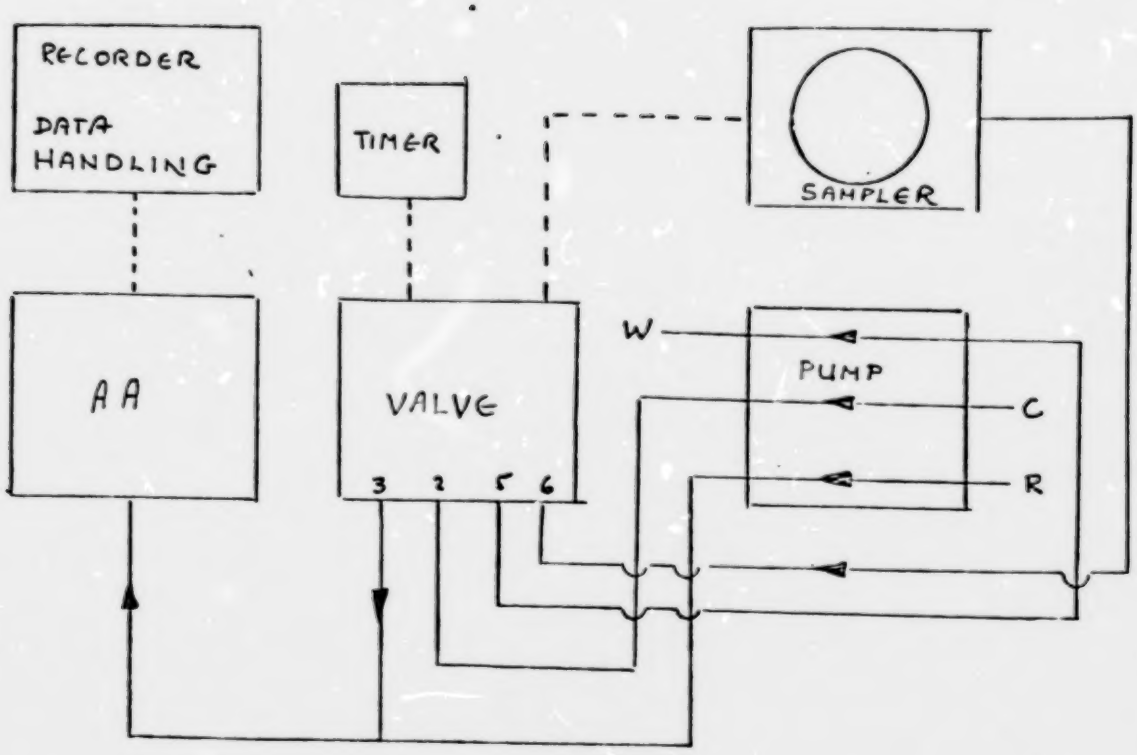


Figure 1

Note 1: See Water Quality manuals for instructions on how to make up these solutions.

Note 2: We reduced the recommended lanthanum solution strengh by a factor of two, thereby increasing operating time of the burner to at least 4 hours, without having to worry about premature lanthanum build-up around the burner slots.

**FLOW INJECTION SYSTEM**

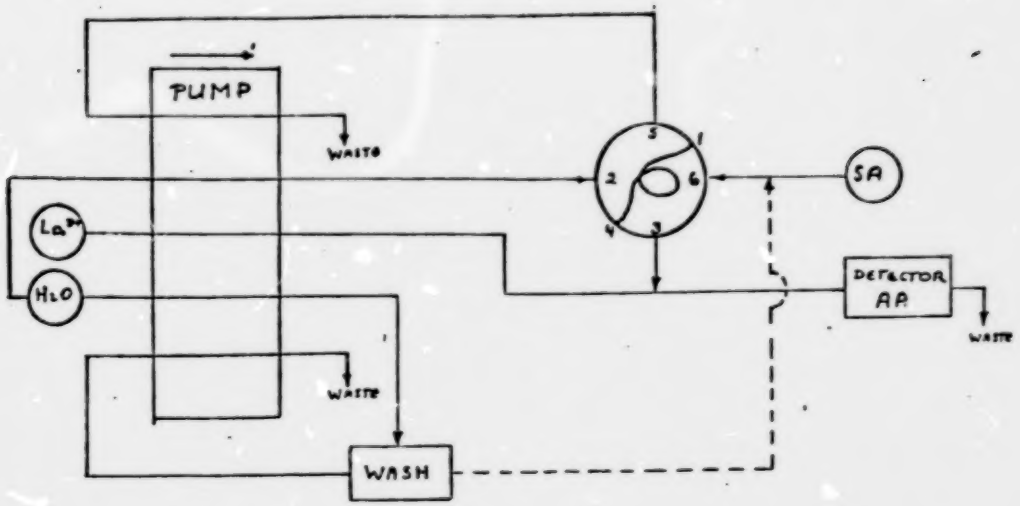


Figure 2 Diagram of Lachat Quik-Chem FIA system interfaced with Perkin Elmer Model 403 Atomic Absorption Spectrophotometer

1. **Tubing Assignments**

| Solution | Tube Colour Code |
|---|---|
| Ca or Mg sample | green |
| Carrier (dist. $H_2O$) | green |
| Reagent (0.25 % $La^{3+}$) | green |
| Wash (dist. $H_2O$) x 2 | blue |

## 2. Lachat Dual Valve Injection Module

The light near each injector port indicates the position of the injector valve; it is "red" when injecting and "green" when loading. The colour of the light must correspond to the mode (INJECT or LOAD) required. To change the position, push the manual injector button(s) once quickly to change the position of the injector valve.

See the Lachat Injector manual for injector port assignments, toggle switch settings for single or dual valve operation (single valve is used in this case), power on/off switch and connection of tubes to valve outlets.

Note: Always make sure the valve is in good working condition. A partially plugged valve and or tube assembly will lead to erratic performance. If problems develop, check the valve first for obstruction, including the connecting tube assemblies.

## 3. Electromatic S-System Recycler-Timer

The timer controls the valve "Load" and "Inject" positions and is set by the two ON and OFF push button range dials. The ranges are from 0 to 99 seconds. It is the "ON" cycle dial (LED on) which has to control the INJECT position of the valve and the "OFF" cycle

dial which must control the LOAD position. The "ON" cycle also must control the length of the wash cycle of the auto-sampler via the valve unit. The timer is connected to the back pannel of the valve unit via the BNC plug.

4. **AA Settings for Ca and Mg for Perkin Elmer 403 Atomic Absorption Spectroscopy**

| Parameter | Setting: Ca | Setting: Mg |
|---|---|---|
| Recorder Full Scale | .25 A | .5 A |
| Recorder Response | 2 or 3 | 2 or 3 |
| Slit | 4 | 4 |
| Wavelength | 422.7 nm | 285.2 nm |
| Oxidant Flow Rate | 65 or 45* | 65 or 45* |
| Fuel Flow Rate | 45 or 30* | 45 or 30* |

*Single Slot Burner.

Note: All tests were done using the impact bead air/acetylene flame, and the "Absorbanc", "10 Average", and "Repeat" modes.

## 5. Miscellaneous Settings

| | |
|---|---|
| Pump Speed | 80 (Lachat Perist. P.) |
| Recorder Range (optim.) | 20 mV |
| Sample Loop Size | 200 microlitres |

Note: The pump speed can be varied from 70 to 90 for optimum performance. Any changes in pump speed will affect injection timing.

Timer Setting:

| | |
|---|---|
| Load Position | 22 to 24s |
| Injection position | 8 to 10s |

Nebulizer: From point of the beginning of suction - one full revolution, which is equivalent to 8 ml of aspiration.

## 6. Peristaltic Pump

All relevant information can be found in the Lachat Quick Chem Systems Manual.

The tubes should be checked occasionally for crushing and replaced if necessary.

To check if a tube is "flowing", briefly lift the suction end out of the liquid. If there is flow, a bubble will result and go up the tube. If there is no flow, investigate where the problem originates.

**CHANGES IN AA OPERATION DUE TO THE FIA INTERFACE**

1. The burner/nebulizer will be aspirating lanthanum at all times due to the continuous flow of reagent solution. Therefore, the burner, aspirator and aspirator tubing may have to be cleaned more frequently than usual. Steadily decreasing peak heights may indicate a clogging problem.
2. Generally, the FIA system will add several feet of extra tubing between sample and the AA. This extra tubing will affect the rate of aspiration. Therefore, during preliminary adjustment of the lamp, burner and nebulizer, the test solution should be aspirated through the running FIA system to get accurate "optimum" adjustments. A constant stream of sample to the burner will be produced if the test is introduced via the "green" tube, which alone bypasses the injector. With the AA and pump running, put the suction end of the green tube into the beaker of test solution and commence with the AA adjustments when the solution reaches the burner. The pump should be running at the recommended rate during these tests.

3. Increasing the pump speed increases the flow rate of liquid to the burner up to a maximum, determined by the maximum rate of nebulization which in turn is determined by the oxidant flow rate. Increasing the pump speed beyond the maximum produces no change in signal magnitude. (See: AA, FIA and miscellaneous settings for Ca and Mg in this manual). The overall flow-rate should be 7 - 8 ml/min. A flow-rate set to high, may lead to leaking around the aspirator tube connection, as the nebulizer will only accept 8 ml/min of delivery maximally at the given nebulizer setting.

**TROUBLESHOOTING**

1. **Bubbles in the Aspirator Line**

Check if none of the reagent bottles is empty and check for leaks in the system. In general, bubbles in the aspirator are less of a serious problem.

2. **Leak in the Flow-System**

There are two types of leaks: Air leaking into the system and liquid leaking from a connection. Air leaks usually occur around the valve due to improper seal. Careful tightening of the three cap screws will cure this problem. If the leak is in a connection, redo

the connection. If the leak persists, it may be due to pressure build up in the lines, possibly due to a clog or misalignment of the ports in the injector. In the latter case, push the manual injector control button (found just below the indicator light) and hold it until a light of the same colour comes up. This indicates that a new injection/load port has been reached. Check for leaks again and repeat the procedure if necessary. If none of the ports are suitable, manual alignment may be needed. For instructions, refer to the troubleshooting section in the Lachat manual.

### 3. Erratic Performance - Poor Reproducibility

Always make sure the valve is in good working order. A partially plugged valve and or tube assembly will cause problems. First check by unscrewing the three cap screws and pull valve apart. Check for obstructions. Also pull apart the rest of the valve assembly lines and "screw" connections and check for obstructions.

### 4. Erroneously Small Peaks

Check to see if the injector position, indicated by the colour of the light, corresponds with the timer position. RED to RED for loading, GREEN to OFF (TIMER) for injection position. The sampler wash cycle must be activated during the inject position.

5. **Sudden Decrease in Signal Height**

Check the tubing system for leaks, particularly in the connections. (See #2 for instructions).

6. **No Flow in the System**

Check if the pressure levers in the cartridges are in the "up" position, and the pump is set at the proper speed with the "MINIMUM" switch off. If no flow is reaching the detector, check that the pump is moving the reagent in the required direction (towards the injector and away from the reagent containers).

APPENDIX II

## High Level

| | Mg (0-20ppm) | | Ca (0-100ppm) | |
|---|---|---|---|---|
| | FIA | WQL | FIA | WQL |
| Control RN | 6.1 | 6.2 | 28.5 | 28.2 |
| Recovery | 102% | 98% | 100% | 101% |
| Duplicates (STD DEV PAIRS) within | .07 | .21 | .43 | .28 |
| between | .09 | .40 | .52 | .68 |
| Replicate | 8.2 | 8.1 | 38.5 | 38.8 |
| C.V. | 1.0% | 1.4% | .3% | .9% |

## Low Level

| | (0-2 ppm) | | (0-10ppm) | |
|---|---|---|---|---|
| Controls | | | | |
| RRL | .10 | (.09) | .44 | .46) |
| RL | .83 | (.79) | 3.71 | 3.73) |
| RRH | 1.36 | (1.29) | 7.34 | (7.24) |
| Recovery | 106 | (97) | 100 | (99) |
| Duplicates (STD DEV) | | | | |
| within | .004 | .006 | .018 | .03 |
| between | .003 | .003 | .024 | .02 |
| Replicates | .249 | .519 | .587 | ~~0.45~~ |
| C.V. | 0.8% | 1.2% | 2.4% | 1.7% |

| | My (0-2) | | Cu (0-10) | | |
|---|---|---|---|---|---|
| | FIA | WQL | FIA | WQL | Proj |
| 12016 | .02 | .02 | 07 | .10 | III |
| 7 | .02 | 02 | 10 | 16 | |
| 8 | .06 | .05 | .20 | 26 | |
| 9 | .06 | .05 | 30 | .34 | |
| 12020 | 1.22 | 1.21 | 5.15 | 5.20 | |
| 1 | 1.82 | 1.54 | 2.33 | 2.21 | |
| 2 | .55 | .53 | 2.56 | 2.62 | |
| 3 | .51 | .50 | 2.20 | 2.31 | |
| 4 | .27 | .26 | 1.03 | 1.06 | |
| 5 | .20 | .18 | 1.12 | 115 | |
| 6 | .72 | 67 | 446 | 431 | |
| 7 | .25 | .24 | 88 | 87 | |
| 8 | .40 | .36 | 2.25 | 2.22 | |
| 9 | .07 | 06 | 59 | .58 | |
| 12030 | .34 | 33 | 87 | 91 | |
| 1 | .17 | 16 | .84 | .86 | |
| 2 | .61 | .59 | 2.14 | 2.17 | |
| 3 | 21 | 20 | .77 | 81 | |
| 4 | .20 | .19 | .83 | .86 | |
| 12035 | .08 | 08 | 38 | .42 | ✓ |
| 13473 | .02 | .03 | (.38) | (11) | 777 |
| 4 | .02 | .02 | .07 | .14 | |
| 13475 | .03 | .03 | .03 | .04 | ✓ |

| | Mg (0-2) | | Ca (0-10) | | |
|---|---|---|---|---|---|
| | FIA | WAL | FIA | WAL | Proj |
| 13476 | .06 | .06 | .11 | .08 | 777 |
| 7 | .01 | .01 | 05 | .03 | |
| 8 | .05 | 05 | .14 | .14 | |
| 9 | .04 | 04 | 21 | .23 | |
| 13480 | .05 | .05 | .24 | .28 | |
| 1 | 10 | .09 | 47 | .47 | |
| 2 | .03 | .03 | 20 | .24 | |
| 3 | .05 | 04 | 20 | .22 | |
| 4 | .02 | .02 | .08 | .10 | |
| 5 | .04 | .03 | .20 | .21 | |
| 6 | 01 | .00 | 03 | .02 | |
| 7 | .01 | 01 | .08 | .09 | |
| 8 | .01 | .01 | 06 | .07 | |
| 9 | .01 | .01 | 03 | .07 | |
| 13490 | .01 | .00 | 03 | .02 | |
| 13491 | .01 | 01 | .03 | .05 | v |
| 18138 | .13 | .12 | 78 | .78 | 775 |
| 9 | .04 | .04 | 36 | .35 | |
| 18140 | .06 | .05 | .25 | .30 | |
| 1 | .42 | .41 | 1.36 | 1.37 | |
| 2 | 20 | .20 | .65 | .65 | |
| 3 | .04 | .04 | .14 | .23 | |
| 18144 | .03 | .02 | .31 | .35 | v |

| | Mg (0-21) | | Ca (0-10) | | |
|---|---|---|---|---|---|
| | FIA | WQL | FIA | WQL | |
| 18145 | .01 | .01 | .03 | .05 | 775 |
| 6 | .01 | .02 | .10 | .12 | |
| 7 | .08 | .07 | .06 | .11 | |
| 8 | .02 | .01 | .12 | 17 | |
| 9 | 02 | .01 | .04 | .11 | |
| 18150 | 01 | .01 | 03 | .02 | |
| 1 | 12 | .11 | .65 | .71 | |
| 2 | 02 | .02 | .08 | .12 | |
| 3 | .25 | .25 | .60 | .65 | |
| 4 | .13 | .13 | .72 | .76 | |
| 5 | .05 | .06 | .21 | .33 | |
| 6 | .02 | .02 | 04 | .12 | |
| 7 | .07 | .07 | .24 | .36 | |
| 8 | .13 | .13 | 1.24 | 1.30 | |
| 9 | .04 | .04 | .06 | .10 | |
| 18160 | .04 | .04 | .11 | .13 | |
| 1 | .04 | .04 | 69 | 71 | J |
| 18162 | .10 | 09 | 06 | .11 | |
| 12034 | 05 | 04 | .17 | .19 | 111 |
| 7 | 23 | 21 | 1.37 | .36 | |
| 8 | .10 | .09 | .47 | .50 | |
| 9 | .03 | .03 | .12 | .15 | |
| 12040 | .15 | .14 | .83 | .84 | J |

Controls

## Mg

| | RRL | RL | RRH | % Recovery |
|---|---|---|---|---|
| 1) | .10 | .83 | 1.36 | 106% |
| 2) | .10 | 83 | 1.34 | 106 |
| 3) | .10 | .83 | 135 | 106 |
| 4) | .10 | .83 | 1.42 | 106 |
| FIA: | .10 | .83 | 1.36 | AVE 106 |
| Exp: WAL | .09 ±.005 | .79 ± .01 | 1.24 ± .02 | 106 (Low) — 106 (High) |

## Ca

| | RRL | RL | RRH | % Recovery |
|---|---|---|---|---|
| 1) | .42 | 3.62 | 7.26 | 100 |
| 2) | .48 | 3.71 | 7.30 | 97.5 |
| 3) | .43 | 3.65 | 7.39 | 102 |
| 4) | .43 | 3.84 | 7.41 | 101 |
| FIA: | .44 | 3.71 | 7.34 | AVE 100 |
| Exp: WAL | .46 ± .01 | 3.73 ± .06 | 7.29 ± .06 | 98 (Low) — 102 (High) |

DATA

TYPE : Precipitation

PARAMETER :

PROJECT(S) :

CRUISE : I.D.# :

| | LAB. NO. | PARAMETER Mg | | PARAMETER PAIR | |
|---|---|---|---|---|---|
| | | | | Mg | |
| | | | | within | between |
| FIA | 12022 | .55 | .55 | | 55 |
| | 12032 | .61 | .62 | | 61 |
| | 13481 | .10 | .10 | | .10 |
| | 18141 | .42 | .41 | | .41 |
| | 18150 | .01 | .01 | | 01 |
| | 18160 | .04 | .04 | | .04 |
| | | | | | |
| | | | | | |
| | | | | | |
| FIA | | Ca | | Ca | |
| | | | | | |
| | | | | | |
| | 12022 | 2.56 | 2.56 | | 255 |
| | 12032 | 2.19 | 2.18 | | 222 |
| | 13411 | .47 | .42 | | .44 |
| | 18141 | 1.36 | 1.34 | | 1.31 |
| | 18150 | .03 | .02 | | 03 |
| | 18160 | .11 | .14 | | .16 |
| | | | | | |
| | | | | | |

| | | STD DEV within | between |
|---|---|---|---|
| Variance of [illegible] | Mg | .004 | .003 |
| Std. Dev. " " " | = | | |
| T Value " " " | = Ca | .018 | .024 |
| Mean Difference | = | | |

Replicate — 27 X F.I.A.

| | Mg | Ca |
|---|---|---|
| 1) | .25 | .60 |
| 2) | .25 | .59 |
| 3) | .25 | .59 |
| 4) | .25 | .59 |
| 5) | .25 | .59 |
| 6) | .25 | .58 |
| 7) | .25 | .58 |
| 8) | .25 | .58 |
| 9) | .25 | .57 |
| 10) | .25 | .57 |
| 11) | .25 | .57 |
| 12) | .25 | .57 |
| 13) | .25 | .56 |
| 14) | .25 | .58 |
| 15) | .25 | .58 |
| 16) | .25 | .58 |
| 17) | .25 | .58 |
| 18) | .25 | .58 |
| 19) | .24 | .60 |
| 20) | .25 | .61 |
| 21) | .25 | .58 |
| 22) | .25 | .60 |
| 23) | .25 | .61 |
| 24) | .25 | .60 |
| 25) | .25 | .60 |
| 26) | .25 | .61 |
| 27) | .25 | .61 |
| | .249 ± .002 | .587 ± .014 |
| C.V. | 0.80% | 2.4% |

STANDARDS:

My

TRAY

| Level | I | II | III | IV |
|---|---|---|---|---|
| 0 | .01 | .01 | .01 | .01 |
| .5 | .48 | .48 | 48 | .49 |
| 1 | 1.01 | 1.00 | 1.00 | 1.00 |
| 1.5 | 1.51 | 1.51 | 1.51 | 1.52 |
| 2.0 | 1.99 | 1.99 | 1.99 | 1.99 |

Cu

TRAY

| Level | I | II | III | IV |
|---|---|---|---|---|
| 0 | .01 | .01 | .00 | .00 |
| 2 | 2.00 | 1.99 | 2.00 | 2.00 |
| 5 | 4.98 | 4.96 | 5.02 | 4.98 |
| 7 | 7.03 | 7.05 | 6.98 | 7.03 |
| 10 | 9.99 | 9.98 | 10.01 | 9.99 |

| | Mg (0-20) | | Ca (0-100) | | |
|---|---|---|---|---|---|
| | FIA | WQL | FIA | WQL | Prob |
| 4/39 | 3.4 | 3.7 | 18.4 | 18.6 | 100's |
| 4/40 | 3.6 | 3.9 | 18.8 | 19.4 | |
| 1 | 3.1 | 3.4 | 14.4 | 14.7 | |
| 4/42 | 2.3 | 2.4 | 12.9 | 13.3 | |
| 4/44 | 3.0 | 3.5 | 21.0 | 21.8 | |
| 4/45 | 4.8 | 5.3 | 22.8 | 23.4 | |
| 4/46 | 4.0 | 4.8 | 19.2 | 21.0 | |
| 5370 | 3.2 | 3.4 | 19.6 | 20.1 | |
| 1 | 3.2 | 3.4 | 17.8 | 18.6 | |
| 2 | 3.4 | 3.8 | 22.5 | 23.3 | |
| 3 | 3.2 | 3.5 | 22.4 | 22.3 | |
| 4 | 2.8 | 3.1 | 9.5 | 15.6 | |
| 5375 | 2.5 | 2.6 | 9.0 | 15.1 | |
| 6197 | 8.1 | 8.6 | 34.9 | 35.8 | |
| 6186 | 8.2 | 8.8 | 38.9 | 38.7 | |
| 6760 | 8.2 | 9.0 | 38.2 | 39.5 | |
| 7582 | 8.0 | 8.8 | 35.5 | 36.2 | |
| 7953 | 8.1 | 9.0 | 35.0 | 35.3 | |
| 7759 | 1.8 | 2.0 | 7.1 | 7.4 | |
| 7966 | 8.1 | 8.9 | 38.3 | 39.8 | |
| 7964 | 8.0 | 8.7 | 37.7 | 37.8 | |
| 9075 | 8.2 | 9.0 | 35.3 | 35.9 | |
| 9080 | 8.2 | 9.0 | 38.1 | 38.5 | |
| 9068 | 8.0 | 9.0 | 35.5 | 35.9 | |
| 2058 | 7.8 | 8.9 | 25.2 | 25.6 | ✓ |
| 6554 | 7.5 | 8.2 | 42.4 | 49.1 | 512 |
| 6555 | 7.7 | 8.4 | 22.6 | 28.2 | ↓ |

| | Mg (0-20) | | Ca (0-100) | | |
|---|---|---|---|---|---|
| | FIA | WQL | FIA | WQL | Proj |
| 06556 | 9.3 | 9.8 | 38.8 | 44.7 | 512 |
| 06557 | 10.2 | 10.2 | 37.1 | 40.2 | |
| 8 | 10.1 | 10.5 | 38.1 | 49.8 | |
| 9 | 7.3 | 7.5 | 46.8 | 55.1 | |
| 06560 | 7.1 | 7.5 | 41.6 | 47.9 | |
| 1 | 7.0 | 7.5 | 44.3 | 49.6 | |
| 2 | 7.0 | 7.2 | 43.6 | 49.2 | |
| 3 | 7.1 | 7.5 | 48.1 | 50.0 | |
| 4 | 7.1 | 7.2 | 51.4 | 55.0 | |
| 5 | 7.2 | 7.5 | 58.8 | 58.7 | |
| 6 | 7.0 | 7.3 | 73.6 | 75.0 | |
| 7 | 6.8 | 7.4 | 34.1 | 35.4 | |
| 8 | 7.1 | 7.1 | 48.6 | 48.6 | |
| 9 | 7.1 | 7.4 | 50.5 | 50.7 | |
| 06570 | 7.1 | 7.1 | 73.5 | 72.9 | |
| 1 | 7.0 | 7.3 | 41.1 | 44.1 | |
| 2 | 7.0 | 7.2 | 52.6 | 52.3 | |
| 3 | 7.1 | 7.5 | 54.5 | 54.6 | |
| 4 | 7.0 | 7.1 | 37.3 | 41.7 | |
| 5 | 7.0 | 7.4 | 40.6 | 43.8 | |
| 6 | 7.1 | 7.3 | 55.2 | 54.3 | |
| 7 | 7.2 | 7.3 | 55.3 | 56.5 | |
| 06578 | 7.1 | 7.2 | 46.7 | 55.1 | |
| 16025 | 12.9 | 12.9 | 41.3 | 42.8 | 300's |
| 16026 | 8.1 | 8.1 | 31.1 | 31.9 | |
| 16401 | 8.6 | 8.8 | 26.5 | 26.9 | |
| 16402 | 5.3 | 5.6 | 22.7 | 22.8 | |

| | Mg (0-20) | | CG (0-100) | | |
|---|---|---|---|---|---|
| | FIA | WQL | FIA | WQL | Proj |
| 16403 | 3.6 | 3.7 | 12.2 | 12.9 | 300 |
| 16404 | 2.8 | 2.8 | 8.6 | 8.8 | |
| 16407 | 5.5 | 5.5 | 23.2 | 24.2 | |
| 16408 | 9.0 | 9.1 | 44.3 | 46.4 | |
| 17050 | 15.4 | 14.9 | 46.0 | 48.5 | |
| 17054 | 6.7 | 6.9 | 19.2 | 21.0 | |
| 5 | 7.9 | 7.8 | 18.4 | 19.8 | |
| 6 | 7.1 | 7.1 | 20.2 | 21.6 | |
| 7 | 12.7 | 12.7 | 40.8 | 43.8 | |
| 8 | 18.4 | 18.0 | 40.8 | 42.6 | |
| 9 | 18.1 | 17.8 | 37.9 | 40.1 | |
| 17060 | 15.6 | 15.0 | 38.6 | 40.3 | |
| 17061 | 11.7 | 11.7 | 34.8 | 38.2 | |
| 17066 | 11.8 | 11.8 | 32.9 | 34.4 | |
| 17644 | — | — | 49.7 | 66.6 | |
| 17650 | 14.0 | 13.7 | 42.7 | 44.4 | |
| 17656 | 19.2 | 18.5 | 44.9 | 45.3 | |
| 7 | 19.7 | 19.2 | 58.3 | 58.0 | |
| 8 | 14.0 | 13.9 | 31.8 | 32.9 | |
| 17659 | 3.3 | 3.4 | 8.5 | 8.9 | |
| 17934 | 14.4 | 14.2 | 43.1 | 43.3 | |
| 17940 | 20.4 | 18.7 | 38.9 | 39.9 | |
| 1 | 17.2 | 16.8 | 41.1 | 41.4 | |
| 2 | 21.8 | 21.3 | 44.0 | 44.1 | |
| 3 | 12.0 | 11.8 | 40.3 | 40.6 | |
| 4 | 12.8 | 12.4 | 40.8 | 37.9 | |
| 17945 | 19.3 | 18.5 | 40.7 | 41.2 | |

| | Mg (0-20) | | Ca (0-100) | | |
|---|---|---|---|---|---|
| | FIA | WQL | FIA | WQL | Proj |
| 16405 | 41.0 | 41.1 | 83.3 | 83.4 | 350 |
| 16406 | 22.0 | 22.6 | 47.2 | 46.4 | |
| 17051 | 24.0 | 27.0 | 55.8 | 57.7 | |
| 2 | 26.0 | 27.3 | 23.7 | 21.5 | |
| 17053 | 21.0 | 21.9 | 25.3 | 33.4 | |
| 17651 | 21.0 | 21.2 | 32.6 | 32.5 | |
| 2 | 63.0 | 64.5 | 76.2 | 77.8 | |
| 3 | 85.0 | 87.1 | 103. | 106. | |
| 4 | 86.0 | 88.3 | 106. | 105. | |
| 17655 | 87.0 | 89.4 | 103. | 105. | |
| 17736 | 46.0 | 47.0 | 76.7 | 76.9 | |
| 7 | 44.0 | 46.3 | 64.8 | 65.5 | |
| 17938 | 49.0 | 51.1 | 62.3 | 61.6 | |
| 15533 | 51.0 | 54.2 | 64.7 | 64.2 | |
| 15971 | 44.0 | 49.1 | 21.7 | 28.8 | |
| 17946 | 18.9 | 18.4 | 40.1 | 41.3 | |
| 7 | 19.1 | 18.3 | 37.0 | 40.5 | |
| 8 | 18.5 | 18.5 | 40.4 | 40.2 | |
| 17949 | 18.9 | 18.5 | 40.7 | 41.3 | |
| 33596 | 8.3 | 8.3 | 39.0 | 38.5 | 102 |
| 7 | 8.0 | 8.2 | 38.8 | 38.3 | |
| 8 | 8.1 | 8.3 | 38.6 | 38.2 | |
| 9 | 8.1 | 8.0 | 38.8 | 38.8 | |
| 33603 | 8.1 | 8.4 | 38.7 | 37.7 | |
| 1 | 8.1 | 8.2 | 38.5 | 38.4 | |
| 2 | 8.1 | 8.2 | 38.6 | 38.6 | |
| 33603 | 8.0 | 8.4 | 38.6 | 37.7 | |

| | My 0-20 | | Cu 0-102 | | |
|---|---|---|---|---|---|
| | FIA | WQL | FIA | WQL | Pro. |
| 33604 | 7.9 | 8.1 | 37.2 | 38.5 | 102 |
| 5 | 8.0 | 7.9 | 37.3 | 39.4 | |
| 6 | 8.0 | 8.0 | 37.6 | 38.8 | |
| 7 | 8.1 | 7.9 | 37.9 | 38.4 | |
| 8 | 8.0 | 7.9 | 37.5 | 37.6 | |
| 9 | 8.1 | 8.1 | 38.2 | 38.3 | |
| 33610 | 8.0 | 7.9 | 37.8 | 38.3 | |
| 1 | 7.9 | 7.7 | 37.8 | 38.5 | |
| 2 | 7.9 | 8.1 | 37.8 | 38.7 | |
| 3 | 7.9 | 7.9 | 38.1 | 38.2 | |
| 4 | 8.1 | 8.2 | 38.4 | 39.2 | |
| 5 | 8.0 | 8.1 | 38.0 | 38.7 | |
| 6 | 7.8 | 7.9 | 38.0 | 38.7 | |
| 7 | 8.0 | 8.2 | 38.4 | 38.5 | |
| 8 | 7.8 | 8.3 | 38.1 | 38.2 | |
| 9 | 7.9 | 7.9 | 38.3 | 38.2 | |
| 33620 | 8.0 | 8.1 | 38.1 | 38.9 | |
| 1 | 8.0 | 7.9 | 38.2 | 38.7 | |
| 2 | 8.0 | 8.2 | 38.5 | 38.8 | |
| 3 | 8.0 | 8.2 | 38.6 | 38.4 | |
| 4 | 8.0 | 8.3 | 39.6 | 40.0 | |
| 5 | 8.2 | 8.0 | 39.4 | 39.4 | |
| 6 | 8.1 | 8.2 | 39.3 | 39.1 | |
| 7 | 8.0 | 8.2 | 39.4 | 38.8 | |
| 8 | 8.0 | 8.0 | 39.6 | 39.6 | |
| 9 | 8.1 | 8.0 | 39.4 | 39.1 | |
| 33630 | 8.0 | 8.2 | 39.4 | 39.8 | |

Controls & % Recovery

FIA

| | My RN | % Rec |
|---|---|---|
| 1) | 6.1 | 102 |
| 2) | 6.0 | 102 |
| 3) | 6.1 | 100 |
| 4) | 6.1 | 100 |
| 5) | 6.0 | 102 |
| 6) | 6.1 | 106 |
| | .1 | |

| L | Ave | H |
|---|---|---|
| 100 | 102 | 106 |

CG

| RN | % Rec. |
|---|---|
| 28.6 | 100. |
| 28.4 | 99.0 |
| 28.7 | 99.5 |
| 28.6 | 99.5 |
| 28.5 | 101. |
| 28.2 | 101. |
| .1 | |

| L | Ave | H |
|---|---|---|
| 99.0 | 100 | 101. |

WQL

| | My | |
|---|---|---|
| 1) | 6.1 | 100 |
| 2) | 6.2 | 98 |
| 3) | 6.2 | 96 |
| 4) | 6.2 | 102 |
| 5) | 6.2 | 92 |
| 6) | 6.1 | 98 |
| | .2 | |

| L | Ave | H |
|---|---|---|
| 92 | 98 | 102 |

CG

| | |
|---|---|
| 27.6 | 101 |
| 28.5 | 100 |
| 28.8 | 100 |
| 27.9 | 101 |
| 28.7 | 103 |
| 27.9 | 99 |
| .2 | |

| L | Ave | H |
|---|---|---|
| 99 | 101 | 103 |

DATA

MATRIX : Water

PARAMETER : Mg

PROJECT(S) :

SOURCE : Level:

| | LAB. NUMBER | PARAMETER Mg PAIR within | | PARAMETER Mg PAIR between | |
|---|---|---|---|---|---|
| EIA | 5370 | 3.2 | 3.2 | 3.1 | 3.1 |
| | 9080 | 8.2 | 8.1 | 8.2 | 8.1 |
| | 6563 | 7.1 | 7.2 | 7.1 | 7.3 |
| | 6578 | 7.1 | 7.1 | 7.1 | 7.2 |
| | 17056 | 7.1 | 7.3 | 7.1 | 7.3 |
| | 17941 | 17.2 | 17.1 | 17.2 | 17.3 |
| | 17946 | 18.9 | 18.8 | 18.9 | 18.7 |
| | 13599 | 8.1 | 8.1 | 8.1 | 8.2 |
| | 33611 | 7.9 | 7.9 | 7.9 | 8.0 |
| | 33626 | 8.1 | 8.0 | 8.1 | 8.1 |
| WQL | 5370 | 3.4 | 3.6 | 3.4 | 3.3 |
| | 9080 | 9.0 | 8.4 | 9.0 | 8.2 |
| | 6563 | 7.5 | 7.2 | 7.5 | 7.2 |
| | 6578 | 7.2 | 7.3 | 7.2 | 7.2 |
| | 17056 | 7.1 | 7.3 | 7.1 | 7.3 |
| | 17941 | 16.8 | 16.9 | 16.8 | 17.1 |
| | 17946 | 18.4 | 19.0 | 18.4 | 18.4 |
| | 13599 | 8.0 | 8.4 | 8.0 | 8.0 |
| | 33611 | 7.7 | 8.1 | 7.7 | 9.0 |
| | 33626 | 8.2 | 8.2 | 8.2 | 9.0 |

| | Std. Dev. within | Std. Dev. between |
|---|---|---|
| Variance of paired differences = | | |
| Std. Dev. " " " = EIA | .07 | .09 |
| T Value " " " = WQL | .21 | .40 |
| Mean Difference | | |

PAIRS

TYPE : Water

PARAMETER : Cu

PROJECT(S) :

CRUISE : INSHORE

| | LAB. NUMBER | PARAMETER Cu PAIR within | | PARAMETER Cu PAIR between | |
|---|---|---|---|---|---|
| FIA | 5370 | 19.6 | 20.2 | 19.6 | 19.8 |
| | 9080 | 38.1 | 38.2 | 38.1 | 37.6 |
| | 6563 | 48.1 | 48.2 | 48.1 | 49.3 |
| | 6578 | 46.7 | 47.6 | 46.7 | 47.8 |
| | 17056 | 20.2 | 21.3 | 20.2 | 21.5 |
| | 17941 | 41.1 | 41.0 | 41.1 | 41.5 |
| | 17946 | 40.1 | 40.4 | 40.1 | 40.6 |
| | 33599 | 37.3 | 37.3 | 37.3 | 38.9 |
| | 33611 | 37.8 | 38.9 | 37.8 | 38.2 |
| | 33626 | 39.3 | 39.1 | 39.3 | 39.4 |
| WQL | 5370 | 20.1 | 21.0 | 20.1 | 21.1 |
| | 9080 | 38.5 | 38.8 | 38.5 | 37.5 |
| | 6563 | 50.0 | 50.2 | 50.0 | 51.1 |
| | 6578 | 55.1 | 55.0 | 55.1 | 56.3 |
| | 17056 | 21.6 | 22.0 | 21.6 | 21.9 |
| | 17941 | 41.4 | 41.5 | 41.4 | 40.5 |
| | 17946 | 41.3 | 40.7 | 41.3 | 40.3 |
| | 33599 | 38.8 | 38.7 | 38.8 | 38.2 |
| | 33611 | 38.5 | 38.3 | 38.5 | 39.2 |
| | 33626 | 39.1 | 39.1 | 39.1 | 40.5 |

| | | STD. DEV. within | between |
|---|---|---|---|
| Variance of paired differences = | | | |
| Std. Dev. " " " | FIA | .42 | .52 |
| T Value " " " | = | | |
| Mean Difference | WQL | .27 | .41 |

STANDARDS

My FIA

| LEVEL | TRAY I | II | III | IV | V | VI |
|---|---|---|---|---|---|---|
| 2 | 2.0 | 1.9 | 1.9 | 1.9 | 1.9 | 1.9 |
| 5 | 4.9 | 4.9 | 4.9 | 5.0 | 5.0 | 5.0 |
| 10 | 10.0 | 10.1 | 10.0 | 10.1 | 10.0 | 10.0 |
| 15 | 15.0 | 14.9 | 15.1 | 15.0 | 15.0 | 15.0 |
| 20 | 20.0 | 20.0 | 19.9 | 20.0 | 20.0 | 20.0 |

My WQL

| | | | | | | |
|---|---|---|---|---|---|---|
| 2 | 2.1 | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 |
| 5 | 5.1 | 5.2 | 5.0 | 5.1 | 5.1 | 5.2 |
| 10 | 10.0 | 9.9 | 10.2 | 10.0 | 9.9 | 10.1 |
| 15 | 14.8 | 15.0 | 14.7 | 15.0 | 15.0 | 14.8 |
| 20 | 20.1 | 20.0 | 20.1 | 20.0 | 20.0 | 20.1 |

Cu FIA

| | | | | | | |
|---|---|---|---|---|---|---|
| 10 | 9.9 | 9.9 | 9.9 | 9.8 | 9.8 | 10.0 |
| 25 | 24.6 | 25.0 | 24.9 | 24.8 | 24.7 | 24.2 |
| 40 | 50.0 | 50.1 | 50.2 | 50.2 | 50.2 | 50.0 |
| 50 | 75.4 | 74.9 | 75.0 | 75.1 | 75.2 | 75.9 |
| 100 | 99.8 | 100.0 | 100.0 | 99.9 | 99.9 | 99.5 |

Cu WQL

| | | | | | | |
|---|---|---|---|---|---|---|
| 10 | 9.9 | 9.9 | 9.9 | 10.0 | 9.9 | 9.9 |
| 25 | 25.0 | 25.2 | 25.6 | 24.8 | 25.0 | 25.1 |
| 40 | 50.2 | 49.6 | 50.2 | 50.1 | 50.6 | 50.4 |
| 50 | 74.8 | 75.4 | 74.2 | 75.0 | 74.3 | 74.4 |
| 100 | 100.1 | 99.9 | 100.3 | 100.0 | 100.3 | 100.2 |

Replicate - 31X

| | Mg | | Ca | |
|---|---|---|---|---|
| | FIA | WQL | FIA | WQL |
| 1) | 8.1 | 8.2 | 38.4 | 38.3 |
| 2) | 8.2 | 8.2 | 38.5 | 38.7 |
| 3) | 8.3 | 8.2 | 38.5 | 38.5 |
| 4) | 8.2 | 8.1 | 38.8 | 39.0 |
| 5) | 8.3 | 8.1 | 38.6 | 38.7 |
| 6) | 8.3 | 8.2 | 38.4 | 38.9 |
| 7) | 8.3 | 8.2 | 38.4 | 38.2 |
| 8) | 8.2 | 8.1 | 38.5 | 39.0 |
| 9) | 8.0 | 8.0 | 38.1 | 39.2 |
| 10) | 8.2 | 8.0 | 38.4 | 39.1 |
| 11) | 8.3 | 8.0 | 38.5 | 38.5 |
| 12) | 8.2 | 8.0 | 38.4 | 39.0 |
| 13) | 8.3 | 8.2 | 38.5 | 39.2 |
| 14) | 8.2 | 8.1 | 38.5 | 38.6 |
| 15) | 8.1 | 8.1 | 38.3 | 39.2 |
| 16) | 8.2 | 8.2 | 38.5 | 38.8 |
| 17) | 8.2 | 8.0 | 38.5 | 38.8 |
| 18) | 8.2 | 7.8 | 38.6 | 39.0 |
| 19) | 8.1 | 8.1 | 38.8 | 38.3 |
| 20) | 8.1 | 8.1 | 38.4 | 39.0 |
| 21) | 8.1 | 7.9 | 38.5 | 38.8 |
| 22) | 8.1 | 8.1 | 38.6 | 39.0 |
| 23) | 8.1 | 8.3 | 38.6 | 38.4 |
| 24) | 8.2 | 8.0 | 38.5 | 38.8 |
| 25) | 8.2 | 7.9 | 38.3 | 39.4 |
| 26) | 8.1 | 8.0 | 38.5 | 38.5 |
| 27) | 8.1 | 8.1 | 38.6 | 38.9 |
| 28) | 8.1 | 8.2 | 38.4 | 39.5 |

| | | | | |
|---|---|---|---|---|
| 29) | 8.2 | 8.1 | 38.5 | 38.4 |
| 30) | 8.1 | 8.0 | 38.5 | 38.8 |
| 31) | 8.1 | 8.1 | 38.5 | 38.9 |
| MEAN ± SD | $\overline{8.2 \pm .08}$ | $\overline{8.1 \pm .11}$ | $\overline{38.5 \pm .13}$ | $\overline{38.8 \pm .33}$ |
| RANGE: | (8.1 - 8.3) | (8.0 - 8.2) | (38.4 - 38.6) | (38.5 - 39.1) |
| C.V: | 1.0% | 1.4% | .3% | .9% |

chemical oceanography, methods 1986

Mee, L.D.
Continuous flow analysis in chemical oceanography: principles, applications and perspectives.
The Science of the Total Environment, 49: p 27 to 87.